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NOTE ON A PERTURBATION THEORY FOR INTERMOLECULAR INTERACTIONS IN THE WAVE OPERATOR FORMALISM

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It is proved that the wave function and energy and their perturbation expansions, given by a wave operator perturbation theory for intermolecular interactions [4], satisfy the conditions necessary to make this theory consistent.

That still a lively interest exists in perturbation theory for intermolecular interactions is shown by some recent papers [1-3], appearing almost simultaneously with this author's most recent publication [4]. It is also evident from the discussions on this subject held at Prof. Hirschfelder's group at the Theoretical Chemistry Institute of the University of Wisconsin this summer (see ref. [3]). On the wave operator theory, proposed by the author, some questions arose, that were not answered in ref. [4]. For this reason we will, in the present note, prove some more properties of this theory. The meaning of the symbols, their definitions and the numbering of equations are the same as those of ref. [4].

1) *The wave function ψ and the energy E , given by the equations*

$$\begin{aligned}\psi &= \psi_0 + TH\psi_0 ; \\ E &= \frac{\langle \psi_0 | H + HTH | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle},\end{aligned}\quad (12)$$

with T defined as

$$T = P[\alpha(1-A) + \beta O + P(E-H)P]^{-1}P, \quad (8)$$

or, alternatively, defined by the equations

$$AT = TA = T; \quad (9)$$

$$OT = TO = 0; \quad (10)$$

$$P(E-H)T = P, \quad (11)$$

satisfy the Schrödinger equation $H\psi = E\psi$.

This is shown as follows:

$$(E-H)\psi = (E-H)A\psi = A(E-H)\psi = O(E-H)\psi + P(E-H)\psi.$$

Treat the two parts separately.

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In the first term, substitute ψ , use (5) and (10) of ref. [4] and substitute the definition of O :

$$\begin{aligned}O(E-H)\psi &= O(E-H)\psi_0 + O(E-H)TH\psi_0 = \\ &= E\psi_0 - OH\psi_0 - OHTH\psi_0 = \\ &= \psi_0 \left[E - \frac{\langle \psi_0 | H + HTH | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} \right].\end{aligned}$$

The expression for E causes this term to vanish identically. In the second part, (5) and (11) are used:

$$\begin{aligned}P(E-H)\psi &= P(E-H)\psi_0 + P(E-H)TH\psi_0 = \\ &= -PH\psi_0 + PH\psi_0 \equiv \\ &\equiv 0\end{aligned}$$

This completes the proof.

2) *The operator T , given by its expansion*

$$T = \sum_{n=0}^{\infty} (PR_0U)^n PR_0P, \quad (19)$$

satisfies (9), (10) and (11).

For (9) and (10) this follows immediately from (5). To prove (11) we substitute the equality

$$(PR_0U)^n PR_0P = PR_0P(U^\dagger R_0P)^n, \quad (a)$$

which is proved in the Appendix of ref. [4] directly from the definitions of P , R_0 and U . Consequently, T can be written as

$$T = \sum_{n=0}^{\infty} PR_0P(U^\dagger R_0P)^n. \quad (19a)$$

Operating with $P(E-H)$ on PR_0P yields, using $HA = AH$ and $PA = P$:

$$\begin{aligned}
P(E-H)PR_0P &= \\
&= P(E-H)AR_0P - P(E-H) \frac{A|\phi_0\rangle\langle\phi_0|A}{\langle\phi_0|A|\phi_0\rangle} R_0P = \\
&= P(E-H)R_0P - P \frac{(E-H)|\phi_0\rangle\langle\phi_0|A}{\langle\phi_0|A|\phi_0\rangle} R_0P.
\end{aligned}$$

Substitute $E-H = E_0-H_0-V$ and use $(E_0-H_0)\phi_0=0$ to obtain:

$$\begin{aligned}
P(E-H)PR_0P &= \\
&= P(E_0-H_0)R_0P - PV'R_0P + P \frac{V'|\phi_0\rangle\langle\phi_0|A}{\langle\phi_0|A|\phi_0\rangle} R_0P.
\end{aligned}$$

As $P(E_0-H_0)R_0P = P$ and the other two terms on the right-hand side just contain U^\dagger , this becomes:

$$P(E-H)PR_0P = P - PU^\dagger R_0P. \quad (b)$$

To prove (11) starting from (19a), one uses the equality (b):

$$\begin{aligned}
P(E-H)T &= \sum_{n=0}^{\infty} P(E-H)PR_0P(U^\dagger R_0P)^n = \\
&= \sum_{n=0}^{\infty} P(U^\dagger R_0P)^n - \sum_{n=0}^{\infty} P(U^\dagger R_0P)^{n+1} = \\
&= P.
\end{aligned}$$

3) In a similar way it is shown that the *different-order perturbation equations*, i.e. the equations satisfied by $\psi^{(n)}$ and $\epsilon^{(n)}$ given by (20), add up to the Schrödinger equation:

$$\begin{aligned}
(E-H)\psi^{(n)} &= (E-H)A\psi^{(n)} = A(E-H)\psi^{(n)} = \\
&= O(E-H)\psi^{(n)} + P(E-H)\psi^{(n)}.
\end{aligned}$$

The two terms are treated separately. The first term gives, for $n \geq 1$:

$$\begin{aligned}
O(E-H)\psi^{(n)} &= O(E-H)(PR_0U)^{n-1}PR_0PV\phi_0 = \\
&= -OH(PR_0U)^{n-1}PR_0PV\phi_0,
\end{aligned}$$

since $OP = 0$. Substitute the definition of O , use $AH = HA$, write $H = H_0 + V$ and remark that the term with H_0 vanishes:

$$\begin{aligned}
O(E-H)\psi^{(n)} &= -\frac{A|\phi_0\rangle\langle\phi_0|HA}{\langle\phi_0|A|\phi_0\rangle} (PR_0U)^{n-1}PR_0PV\phi_0 = \\
&= -A\phi_0 \frac{\langle\phi_0|V(PR_0U)^{n-1}PR_0PV|\phi_0\rangle}{\langle\phi_0|A|\phi_0\rangle} = \\
&= -\epsilon^{(n+1)}A\phi_0.
\end{aligned}$$

For $n = 0$:

$$O(E-H)\psi_0 = [E - E_0 - \epsilon^{(1)}]A\phi_0.$$

Adding the equations for $n=0, \dots, \infty$ yields:

$$O(E-H)\psi = [E - E_0 - \epsilon^{(1)} - \epsilon^{(2)} - \dots]A\phi_0 \equiv 0.$$

The second term gives, for $n \geq 1$,

$$P(E-H)\psi^{(n)} = P(E-H)(PR_0U)^{n-1}PR_0PV\phi_0,$$

which becomes, upon using (a) and (b):

$$\begin{aligned}
P(E-H)\psi^{(n)} &= P(E-H)PR_0P(U^\dagger R_0P)^{n-1}V\phi_0 = \\
&= P(U^\dagger R_0P)^{n-1}V\phi_0 - P(U^\dagger R_0P)^nV\phi_0.
\end{aligned}$$

For $n = 0$,

$$P(E-H)\psi_0 = -PV\phi_0.$$

Adding the equations for $n = 0, \dots, \infty$ yields:

$$P(E-H)\psi = PV\phi_0 - PV\phi_0 \equiv 0.$$

If these results are added again, the Schrödinger equation is obtained:

$$\begin{aligned}
0 &= O(E-H)\psi + P(E-H)\psi = A(E-H)\psi = \\
&= (E-H)A\psi = (E-H)\psi.
\end{aligned}$$

With the completion of these proofs the theory becomes entirely consistent; the wave function and energy resulting from it do indeed satisfy the Schrödinger equation; their expansions satisfy perturbation equations that add up to the Schrödinger equation.

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COMMENT ON VAN DER AVOIRD'S WAVE OPERATOR FORMALISM

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In regard to the papers on the perturbation theory of forces by Van der Avoird [1,2], it is worthwhile to point out that *if* the matrix PR_0P , defined * by eqs. 5 and 14, does *not* have an inverse in the space P , then the proposed solution will not satisfy the original Schroedinger equation. This follows since the set of equations

$$PR_0P(E-H)PT = PR_0P$$

will not have a unique solution, and the inverse of $PR_0P(E-H)P$, expressed as an expansion in eq. 19, will not exist.

For the case when E_0 is the ground state of H_0 , the R_0 is negative definite so that PR_0P has

* Here the equation numbers and notation are those of ref. [1].

an inverse and there is no difficulty **. For excited states R_0 is no longer a definite operator so that the inverse of PR_0P might not exist. Although a slight change in the definition of H_0 would correct for this, convergence problems due to this difficulty may occur in the application of the theory to excited states.

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** Preliminary calculations on the ground states of some simple potentials have shown that the theory gives reasonable results.